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PERSISTENCE OF TELODRIN AND DDT ON SWEET CORN AS DETERMINED BY GAS CHROMATOGRAPHY[1/]

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Telodrin (1,3,4,5,6,7,8,8-octachloro-1,3,3a,4,7,7a-hexahydro-4-7-methanoisobenzofuran) has been shown to be effective in controlling insects that attack sweet corn. In field experiments at Tifton, Ga., sweet corn treated with 1 pound of Telodrin per acre resulted in significantly better control of corn earworm (Heliothis zea (Boddie)) and the dusky sap beetle (Carpophilus lugubris Murray) than did DDT at 2 pounds per acre. Henderson et al.[2/] reported that Telodrin granules (0.4 pound per acre) gave 83-percent control of the fall armyworm (Laphygma frugiperda (J. E. Smith)) on sweet corn and 71-percent on grain sorghum for 7 days. An emulsifiable formulation of this insecticide applied at the same rate produced complete control up to 3 days and 68- and 43-percent control for 7 days on sweet corn and grain sorghum, respectively. Before the use of Telodrin on sweet corn can be recommended, however, data must be available regarding its persistence on this crop. The present study was conducted to obtain such data. This report is a summary of research conducted and should not be considered as a recommendation of any treatment discussed.

Guthrie and Bowery[3/] reported the persistence of Telodrin on green tobacco analyzed by a bioassay method of Sun and Sun.[4/] Bioassay procedures, however, do not generally provide the specificity and high reproducibility desired in residue determinations and are used primarily in the absence of specific chemical methods. For this reason, an alternate analytical procedure was sought for the determination of Telodrin residues on sweet corn.

1/ Mention of a proprietary product in this publication does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval by the Department to the exclusion of other products that may also be suitable.

2/ Henderson, C. F., Kinzer, H. G., and Hatchett, J. H. Insecticidal field screening tests against the fall armyworm in sorghum and corn. Jour. Econ. Ent. 55: 1005-1006. 1962.

3/ Guthrie, F. E., and Bowery, T. G. Thiodan and Telodrin residues on tobacco. Jour. Econ. Ent. 55: 1017-1018. 1962.

4/ Sun, Y.-P., and Sun, S.-Y. T. Microbioassay of insecticides with special reference to aldrin and dieldrin. Jour. Econ. Ent. 45: 26-37. 1952.

The principle of electron-capture detection in gas chromatography is amenable to the analysis of residues of Telodrin and other chlorinated hydrocarbon pesticides, as reported by Goodwin et al.5/ When this principle is used with suitable sample preparation and chromatographic conditions, it provides a specific and ultrasensitive method with high reproducibility. This procedure was employed for the simultaneous determination of residues of Telodrin and p,p'-DDT.

Application of Insecticide

A field of Royal Gold sweet corn, treated 12 days previously with 2 pounds of technical DDT per acre as an emulsifiable concentrate to control a heavy infestation of the fall armyworm, was divided into four blocks. Each block consisted of 16 rows, each 100 feet long, with 3 feet between rows. The plants were about 1 foot apart. Each block was further divided into four equal plots consisting of four rows each, and the blocks were arranged in a randomized-block design, which provided four replications for each of three treatments and a control plot for each replication.

Single applications were made with an emulsifiable concentrate of technical Telodrin on August 20, 1962, when the corn was in the 95-percent silk stage, at rates of 0.5, 1, and 2 pounds per acre. Applications were made with a high-clearance corn sprayer moving at 4 miles per hour. A pressure of 100 p.s.i. was used to deliver 50 gallons of water per acre from four 65° fan-type nozzles per row.

The weather at the time of application was as follows: Temperature, 90° F.; wind velocity (measured 2 feet off the ground), 0-1 m.p.h.; relative humidity, 45-50 percent; clear skies and no precipitation.

Sampling

Field samples for each plot consisted of 10 plants selected at random from the two center rows and taken at 0, 1, 2, 4, 7, 15, and 21 days after the application of Telodrin. The corn was allowed to dry after the insecticide application before the initial samples were taken. The plants from each plot were further divided as follows and chopped in a silage cutter in this order: (1) Ears, (2) ear husks, and (3) stalks and leaves. The sequence for chopping samples within a group was such that none were preceded by a sample from a higher rate of treatment. The silage cutter was thoroughly washed after use for each group.

Sample Extraction and Cleanup

A representative 500-g. portion of each sample was tumbled with 1,000 ml. of redistilled hexane for 1 hour. The hexane extract was then filtered, and a 500-ml. aliquot, representing 250 g. of the sample, was concentrated to about 25 ml. on a steam bath by using a jet of dry air.

5/ Goodwin, E. S., Goulden, R., and Reynolds, J. G. Rapid identification and determination of residues of chlorinated pesticides in crops by gas-liquid chromatography. Analyst 86 (1028): 697-709. 1961.

The cleanup of extracts was performed in a 2-cm. i.d. chromatographic column packed with 8 g. of a Florisil-Celite 545 mixture (5:1, w/w), with a 1-inch layer of anhydrous sodium sulfate on top of the adsorbent. The column was washed twice with 25-ml. portions of hexane, which were discarded; then the 25 ml. of concentrated plant extract was added and allowed to percolate into the adsorbent. The walls of the column were washed with two small portions of hexane that were separately allowed to percolate into the adsorbent. The insecticides were then eluted with sufficient hexane to yield approximately 250 ml. of eluate. The eluate was finally made to a volume of exactly 250 ml. This volume of hexane removed essentially all the Telodrin and DDT from the adsorbent, as demonstrated by ultraviolet spectrometry and confirmed by gas chromatography.

Gas Chromatography

A Jarrell-Ash, Model 700, Universal Chromatograph, equipped with a 10-millivolt Bristol recorder, disk-chart integrator, and an electron-affinity detector containing 100 mc. of tritium as TiH_2^3, was used in this investigation. The detector was operated at 17 volts with an instrument-range setting of 10^{-9} amperes. The maximum millivolt output was attenuated by 3 1/3 (position 3) to stabilize the baseline. The time-constant position "Res" was used to provide immediate recorder response to the amplified signal. The column was operated isothermally at 180° C., and the detector and injection port were each set at 200°. Although the sample splitter was not employed, its heater was set at 195°.

The U-shaped column consisted of 2 feet of 1/4-inch o.d. stainless-steel tubing. The packing (3.15 g.) consisted of Dow Corning High Vacuum Silicone Grease (5 percent w/w) on acid-washed Chromosorb W (80-100 mesh). The purification procedure used for the liquid phase and its support is described by Burke.6/ The column was packed with the aid of a vibrator, and a small plug of glass wool was inserted at each end. After the column was conditioned at 225° C. for about 20 hours with a dry-nitrogen flow of about 200 ml. per minute, it was allowed to cool and then connected to the detector. The instrument was equilibrated to the operating conditions already described, and the dry-nitrogen flow was regulated to 145 ml. per minute (outlet) at a pressure of 14 p.s.i. (inlet). The standing current under these conditions was about 4.2×10^{-9} amperes.

The chromatography of a series of standard Telodrin solutions established a retention time of 2.7 minutes for this insecticide. The peak area was directly proportional to the concentration, provided the quantity injected did not exceed 1.4 ng. (1.4×10^{-9} g.). A peak area of 790 integrator counts was obtained with 1.0 ng. of Telodrin, and the smallest detectable quantity was about 5 pg. (5×10^{-12} g.). The retention time for p,p'-DDT was 8.7 minutes, and the area-concentration proportionality relationship held for quantities up to about 5 ng. An injection of 1.0 ng. of p,p'-DDT produced a peak area of 570 integrator counts, and the smallest detectable quantity was about 10 pg. The retention time for o,p'-DDT, a constituent of technical DDT, was 6.7 minutes; 1.0 ng. produced a peak area of 500 integrator counts; and the smallest detectable quantity was about 12 pg. On our instrument an area of 1 $cm.^2$ was equivalent to about 190 integrator counts.

6/ Burke, Jerry. Preparation of Chromosorb, silicone grease column for Dohrmann Microcoulometric Gas Chromatograph. U.S. Dept. HEW Bureau By-Lines 4 (1): 1-6. 1962.

Samples of hexane extract for injection (5 µl.) were taken either directly from the 250 ml. of eluate from the Florisil-Celite column or after an appropriate dilution of the eluate. The gram equivalent of corn analyzed ranged from 1.0×10^{-4} to 5.0×10^{-3}, depending on the concentrations of Telodrin and DDT present in a particular sample.

Recoveries of Telodrin added to hexane extracts prior to the Florisil cleanup were found to be essentially 100 percent in the range of 0.01 to 100 p.p.m., and duplicate analyses checked within $\pm$ 2 percent. Therefore, corrections were not made for recovery, and internal standards were not employed. Standard insecticide samples were analyzed daily, however, because the repeated injection of corn extracts gradually reduced the sensitivity of the detector. The insecticide content was calculated by relating the peak areas of the unknowns to those of standards analyzed on the same day. The sensitivity of the detector was restored by injecting several 2-ml. portions of hexane, but injection was made only after the response had dropped from 10 to 15 percent, because several hours were required for the instrument to again attain equilibrium.

After about 280 injections of the corn extracts, instability of the baseline and tailing of the peaks became noticable, which necessitated the installation of a new column.

Results and Discussion

In figure 1, gas chromatogram A demonstrates that the hexane extracts of sweet corn did not interfere with the analysis of Telodrin and p,p'-DDT. Absence of plant interference eliminated the necessity for analyzing control samples, since any response at 2.7 or 8.7 minutes is due to the insecticides (chromatogram B). The slight response obtained during the interval of 21 to 24 minutes resulted from hexane impurities. Figure 2 is a gas chromatogram of a typical sample analyzed during the investigation. The small peak at 6.7 minutes is o,p'-DDT and the one at 5.4 minutes is an impurity from the technical DDT application.

Samples taken from control plots a few hours after the Telodrin was applied were analyzed and the following levels were obtained: Stalks and leaves, 0.17-0.46 p.p.m.; ear husks, 0.03-0.06 p.p.m.; and ears, 0-0.01 p.p.m. These residues, identified as Telodrin, probably resulted from drift during spraying operations in the field. Since it was previously established that hexane extracts of untreated sweet corn did not interfere with the analysis of Telodrin or DDT (fig. 1), no further control samples were analyzed.

Residue data for Telodrin are given in table 1. Very low levels (0-0.03 p.p.m.) of Telodrin were detected in the ears, but because of their infrequent and erratic appearance they are attributed to contamination, possibly during the sampling process. Residues of Telodrin were much lower on the ear husks than on the stalks and leaves, and in general these levels varied directly with the rates of application. However, some deviation from this trend occurred on the ear husks, and this deviation may have been partly caused by the variation in size of the immature ears at the time of application. The persistence data obtained from the stalks and leaves are believed to more nearly reflect the true behavior of Telodrin on sweet corn. The amounts of Telodrin residue on these two groups of plant parts at any time interval were essentially a function of the concentration of insecticide applied.

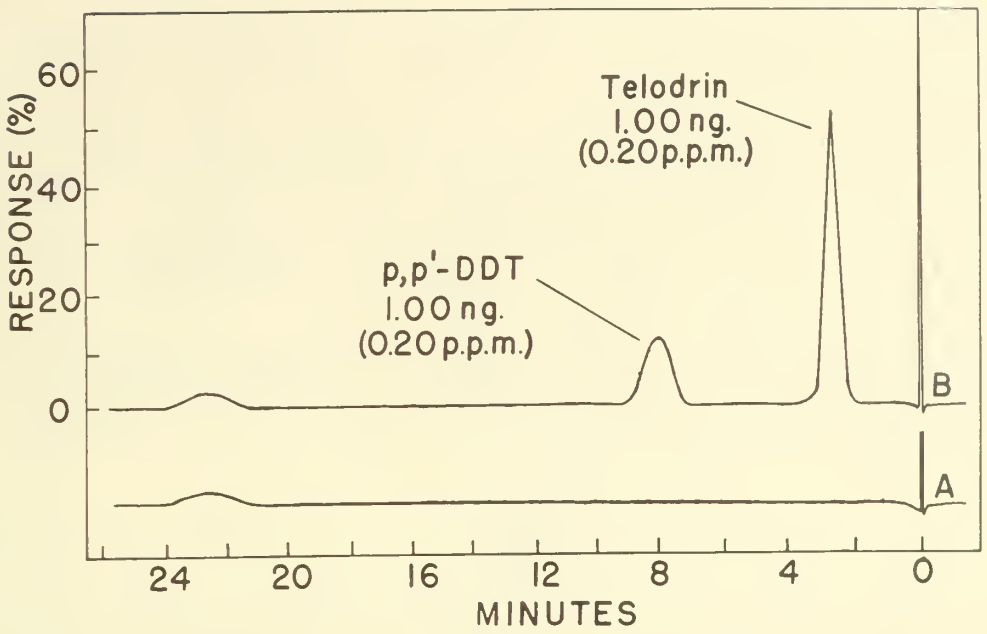

Figure 1.--Gas chromatograms: (A), Hexane extract equivalent to 5.0 x 10^{-3} g. of stalks and leaves from greenhouse sweet corn free of insecticides; (B), extract A fortified with Telodrin and p,p'-DDT.

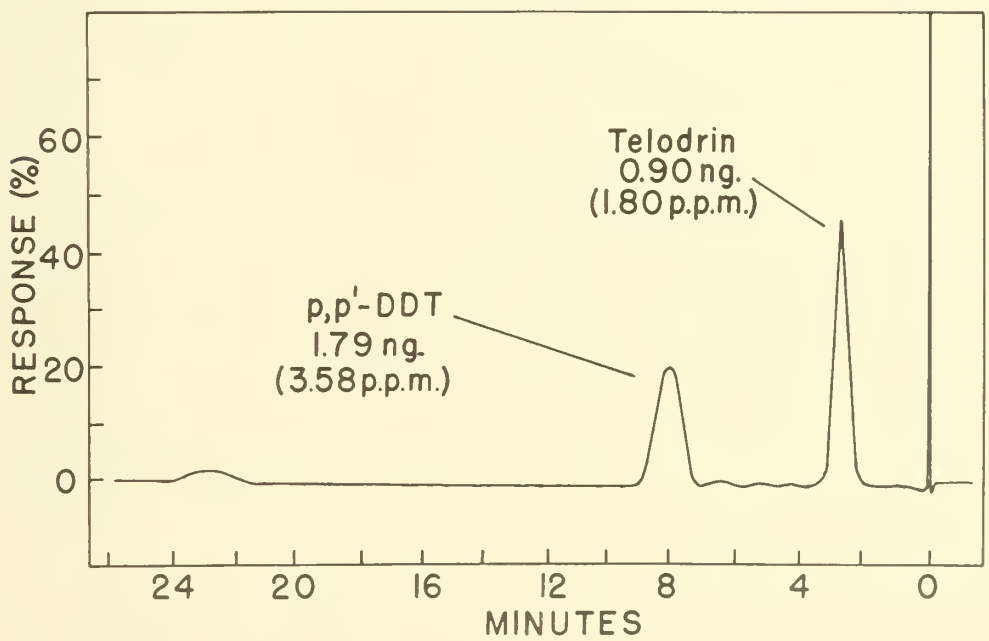

Figure 2.--Gas chromatogram from extract equivalent to 5.0 x 10^{-4} g. of stalks and leaves sampled 4 days after treatment with technical Telodrin (1 pound per acre) and 16 days after application of technical DDT (2 pounds per acre).

The residue data for p,p'-DDT, as shown in table 2 followed the same general trend, but DDT was much more persistent. The stalks and leaves still retained 2.30 p.p.m. after weathering in the field for 33 days. The low levels of DDT on the ear husks were expected, since the corn was very immature at the time of the DDT application. Only the p,p'-DDT is reported in table 2 because the o,p'-isomer was not present in measurable amounts in samples with extremely low residues. Samples containing sufficiently high residues to permit accurate measurement of the o,p'-isomer demonstrated that this isomer was consistently about 8.1 percent of the DDT present at all sampling intervals.

These tests demonstrated that the use of Telodrin or DDT under the conditions of the experiment did not cause residues in the corn ears. Significant residues of Telodrin and DDT remained on the forage, however, for 21 and 33 days, respectively, after application.

Summary

The persistence of Telodrin (1,3,4,5,6,7,8,8-octachloro-1,3,3a,4,7,7a-hexahydro-4,7-methanoisobenzofuran) applied at the rates of 0.5, 1, and 2 pounds per acre and DDT at 2 pounds per acre was determined in the ears, on the ear husks, and on the stalks and leaves of sweet corn. An ultrasensitive analytical method of high reproducibility and specificity, employing gas-liquid chromatoggraphy with electron affinity detection, was used for the simultaneous determination of both residues. Residues of Telodrin and DDT still remained 21 and 33 days, respectively, after application on the husks and on the stalks and leaves, but no residues were present in the ears of sweet corn with husks removed.

Table 1.--Residues of Telodrin on sweet corn plants after field applications of emulsifiable concentrate at different rates

Days after application	Rainfall (inches)[1]	Telodrin residues (p.p.m.)[2] at indicated rate of application (pounds per acre)								
		Stalks and leaves			Ear husks			Ears		
		0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
0	--	1.88	3.38	8.42	1.90	1.96	1.80	0.00	0.00	0.01
1	0.0	1.25	2.06	2.74	.71	.69	1.37	.00	.00	.00
2	.0	.82	1.56	2.05	.38	.51	.93	.00	.00	.00
4	.5	1.04	1.16	2.09	.16	.29	.50	.00	.00	.00
7	1.0	.50	.81	1.34	.28	.38	.65	.00	.00	.01
15	.0	.43	.72	.95	.14	.29	.54	.00	.00	.01
21	.7	.23	.52	.70	.07	.13	.23	.03	.00	.00

1/ Between sampling.

2/ Mean of four replications.

Table 2.--Residues of p,p'-DDT on sweet corn plants after field applications of emulsifiable concentrate at 2 pounds per acre

Days after application	Rainfall (inches)[1]	p,p'-DDT residues (p.p.m.)[2]		
		Stalks and leaves	Ear husks	Ears
12	(3/)	4/4.21	(5/)	(5/)
13	0.0	4.32	0.24	0.01
14	.0	3.90	.23	.00
16	.5	3.98	.22	.01
19	1.0	3.06	.21	.01
27	.0	2.89	.23	.00
33	.7	2.30	.12	.01

1/ Between samplings.

2/ Mean of 12 replications except as noted.

3/ Rainfall during 0- to 12-day interval totaled 1.8 inches.

4/ Mean of 8 replications.

5/ Not analyzed.

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